Catalytic Properties of ZSM-5 based Cu-Zn Catalysts Applies to Ethanol Synthesis from Syngas

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Abstract. Cu-Zn catalysts based on ZSM-5 were prepared with impregnation method. Their catalatic behaviors for the synthesis of ethanol from syngas were investigated in a fixed bed. XRD and H_2-TPR were adopted to characterize the structure and of the catalysts. In the synthesis procession, such factors as ZSM-5 with varied n(Si)/n(Al) ratio, reaction temperature and space velocity were inspected carefully. The results showed that: changing the ratio of silica to alumina in the carrier zeolite has a great influence on the conversion of CO.with a n(Si)/n(Al) ratio of 80, the conversion rate of CO peaked at 25% and the selectivity to ethanol reached 22%. Optimal space velocity for Cu-Zn catalysts was 8400·mL^{-1}·h^{-1}·g^{-1}.

1. Introduction

The synthesis of ethanol from syngas is in line with China's energy resources conditions due to ample sources of raw materials. This method has a prosperous future. There are four kinds of catalysts commonly used in the synthesis of ethanol. Rhodium based catalysts reported in the literature[1-2]exhibited a high catalytic selectivity for C_2 oxygenates. However, this kind of catalysts could hardly be applied to industrial production due to the limited reserves of rhodium and its expensive cost. Modified methanol catalysts include two sorts for either the high-pressure reaction or the low-pressure methanol synthesis[3-8]. Modified methanol catalysts performed are low ethanol selectivity. Modified Fischer-Tropsch synthesis catalysts were made by dislocating the traditional Fischer-Tropsch synthesis catalysts (Fe, Co, Ni) onto the carrier prepared through various preparation methods[9-12]. It is reported that such catalysts shows a low level of ethanol production rate with much more deputy product like hydrocarbon. The main representatives of Molybdenum-based catalysts are MoS_2-based catalysts[13]. The total alcohol selectivity, primarily for linear alcohols in the product, may reach 75%~90%.

Copper-based catalysts have showed high activity and selectivity in the synthesis of DME or methanol, applied in the industrial production in the fixed reaction bed. This

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subject conducted a serious of experiments, aiming at improving the properties of ZSM-5 based Cu-Zn catalysts. A dipping method was used in preparation of samples.

The micro structure of ZSM-5 zeolite can be described as the staggering of SiO_4 and AlO_4 tetra-hedras to a certain ratio, containing unique three-dimensional straight channels and Zigzag-type channels, which contribute to its excellent selected reaction catalytic effect[14]. However, applying ZSM-5 to the synthesis of ethanol can be rarely seen in state-of-art literature.

2. Experimental.

According to n(Si)/n(Al)/n(TPABr)=M: 1: 4, where, M = 25,50,80,100, a certain amount of aluminum isopropoxide, ammonia, tetrapropylammonium bromide were mixtured into water solution, then stirring the solution and adding TEOS slowly. The pH was adjusted to 11. Resultant solution was poured into a hydrothermal reaction kettle at 160 ^{o}C and crystallized for a certain time. The products ZSM-5 molecular sieves were acquired by centrifuging and it was washed several times with distilled water. After that, the products were placed in an oven, and dried at 120 ^{o}C for 10h. Samples were stored in the desiccator.

Using $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $RhCl_3 \cdot nH_2O$ as metallic precursor, according to n(Cu):n(Zn):n(Rh)=2:1:0.05, controlling the total loading capacity of copper, zinc and rhodium at 5wt%, mixed nitrate solution with copper and zinc anions was prepared. Dried ZSM-5 molecular sieves were added into prepared metallic solution, the amount of which was same to molecular sieve's saturated water absorption volume. The mixture was treated under ultrasound for 1h. Then the dipping lasted for 24h. Maintained mixture was baked at 100^{o} C for 6h and then at 350^{o} C for 5h. Baked products were grounded and sieved to obtain Cu-Zn/ZSM-5 catalysts with n(Al)/n(Si) of 25, 50, 80 or 100 respectively and these catalysts were referred to as C-25, C-50, C-80, C-100.

The ethanol synthesis from syngas was carried out in a fixed-bed continuous flow micro-reactor. Gas products directly went into the GC-9560 gas chromatograph.

XRD experiments was conducted via Empyrean type high-temperature X-ray diffractometer (produced by Holland PANalytical B.V.Company).

H_2-temperature programmed reduction. PX200 catalyst characterization system was chosen to carry out temperature-programmed reduction characterization.

3. Results

The effects of Si/Al molar ratio was investigated with following experiments: 5wt% catalysts was loaded onto four kinds of molecular sieves with n(Si)/n(Al) = 25,50, 80,100 respectively by impregnation method. Molar ratio n(Cu)/n(Zn)/n(Rh)=2: 1: 0.06. Resultant catalysts were designated as C-25, C-50, C-80, C-100; Experimental conditions in the reactor were set as: 1g catalysts, T = 533K, t = 72h, CO: H_2 = 1: 2, GHSV = 8400$\cdot mL^{-1} \cdot h^{-1} \cdot g^{-1}$.The results are shown in Figure 1 to 2.

As can be seen from figure 1, conversion rate of CO increased with reaction time. C-80 showed the maximum conversion rate of CO, peaking at 25%, higher than figures provided by the other three catalysts(C-80> C-50> C-25> C-100). That is to say, too low or too high n(Si)/n(Al) ratio in Cu-Zn / ZSM-5 catalysts was not conducive to improve the conversion of CO. Fig. 2 illustrated that C-80 exhibited highest ethanol selectivity of 22%. Since the Si-O bond (0.164nm) was shorter than the Al-O bond (0.175nm), larger amount of silica tended to affect crystallization in an adverse way.

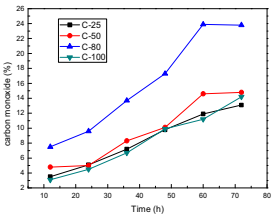

Fig. 1 Effect of different catalysts for CO conversion

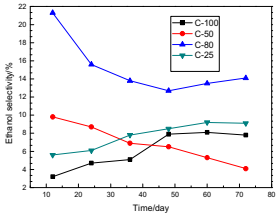

Fig. 2 Ethanol selectivity of different catalysts

The effects of GHSV on CO conversion and Ethanol selectivity were shown in figure 3 .

Sample C-80 was taken to pursue single-factor experiments. As shown in fig 3, as the gas hourly space velocity increased, CO conversion rate gradually decreased while the selectivity to ethanol gradually increased. GHSV lower than 8400·mL^{-1}·h^{-1}·g^{-1} has little impact on the conversion rate of reactants . However, a higher GHSV greatly limited the contact time for the reactants and the catalysts, which was unfavoured by reaction molecules adsorbed by the catalysts. As a result, the conversion of CO reduced significantly[15].

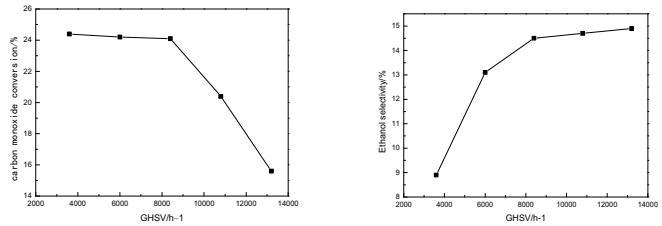

Fig. 3 The effects of GHSV on CO conversion and Ethanol selectivity

4. Discussion

Fig. 4 shows XRD patterns of different catalysts. As it can be seen, all of these four molecular sieves obvious characteristic diffraction peaks at 2θ=7.9°, 8.7°, 22.8°, 23.9°, 24.5° indicating the MFI structure . diffraction peaks appearing at 2θ= 29.8°, 35.6°, 35.8°, 38.8° indicated that the Cu existed in the catalysts in the form of Cu_2O or CuO. This was partly resulted from insufficient reduction. Another reason may be the small particle size or highly dispersion of Cu. Increasing the ration of n(Si)/n(Al) was in line with an enhanced intensity of the diffraction peaks. This phenomenon indicated that higher n(Si)/n/(Al) promoted crystallization of the catalysts.

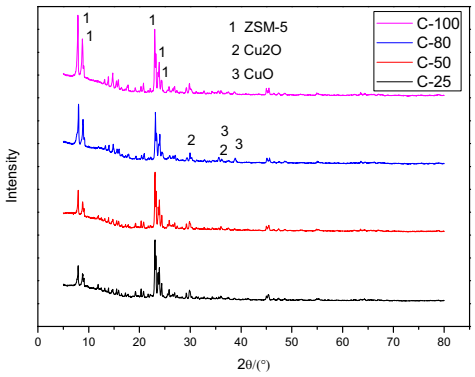

Fig. 4 XRD patterns of different catalysts.

H_2-TPR profiles for all catalysts were showed in figure 10. As for samples C-25 and C-50, the first hydrogen consumption peaks appeared under 343K and 493K, which could be attributed to the reduction of $CuO \rightarrow Cu^0$according to the XRD results. A larger n(Si)/n/(Al) contributed to a higher reduction temperature. C-100 showed only one reduction peak, indicating a smaller amount of CuO in the catalysts resulted by the shrinkage of cells. The other possible reason may be the reduction of Cu monoxides under complex experimental conditions.

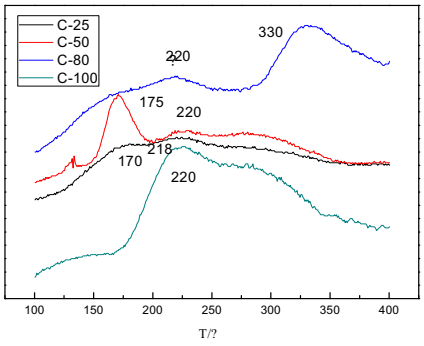

Fig. 5 H_2-TPR Characterization of different catalysts

5. Summary

Obtained Cu-Zn/ ZSM-5 catalysts in this project showed higher catalytic activity. Worth to be mentioned, catalysts with n(Si)/ n(Al) of 80 performed the highest catalytic activity in the synthesis of ethanol from syngas.With a reaction temperature of 533K and GHSV lower than $8400 \cdot mL^{-1} \cdot h^{-1} \cdot g^{-1}$, CO conversion rate reached 25% and was hardly influenced by GHS Velocity.

6. Acknowledgements

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